

INVESTIGATION OF THE PRODUCTION OF GAS OIL OF LOW AROMATIC CONTENT

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The demand on gas oil of low aromatic content was increasing significantly in the last years. The reasons of this the more and more stricter quality requirements of diesel fuels, partly the extending use of these products as good quality feedstocks of steam cracking for producing light olefins. In Hungary, the growing demand on gas oil of low aromatic content is expected in the near future. Its reason is that the restriction of the polyaromatic content of diesel fuels came into force in the European Union in the year 2000 and the assumed growing in the quantity requirements of ethylene and propylene may cause extended inquiry for this base stock.

The experimental results of producing gas oil of low aromatic content are presented. In the first step of the dual stage process the sulphur content of the gas oil was reduced (≤ 10 ppm), in the second one the hydrodearomatization of the product on Pt/Al₂O₃ catalyst was studied. The effects of the process parameters (temperature, LHSV, pressure, etc.) on the yield and product quality are discussed. On the base of experimental results the advantageous key process parameters were determined. The possible applications of the obtained gas oils as diesel fuel blending components and the feedstock of the steam cracking were examined.

Keywords: hydrodearomatization, gas oil, emission reduction, steam cracking feed, noble metal catalyst

Introduction

The restriction of the exhaust gas emission (CO, SO₂, NO_x, particulate matter) have been kept stricter in Europe (for example the emission limits of light duty diesel engines are given in *Table 1*) and other parts of the world [1, 2, 3, 4, 5, 6].

To satisfy all requirements is only possible by developing of engine construction, improving the quality of fuels and using exhaust gas treating system (oxidizing catalysts, particle filters, NO_x-trap) [7, 8, 9, 10, 11]. The present and the future quality requirements of diesel fuels are summarized in *Table 2*.

From the aspect of exhaust gas emissions of the diesel engine very important compounds are the aromatics, mainly the polyaromatics, which have carcinogenic effect in themselves, further the soot originating from the partial burning of these compounds in the engine are carcinogen as well [12, 13, 14, 15].

Besides the human health and environmental effects the aromatic compounds may cause problems in the engine because they have low cetane number.

In addition to diesel fuel the petrochemical industry uses gas oil in growing quantity as base stock of steam

cracking, where the aromatic compounds have also harmful effect, as they increase the quantity of the less valuable fuel oil, tar and coke [16, 17].

The aim of the present study was to identify and quantify the key process parameters for the hydrodearomatization (HDA) of a previously hydrodesulphurized gas oil fraction on Pt/Al₂O₃ catalyst. We studied the effects of key process parameters on the saturation of aromatic compounds. On the basis of the experimental results the advantageous process parameters were determined.

The obtained products were qualified from the point of view using them as blending components of diesel fuel and feedstock of steam cracking.

Experimental

The experiments were carried out in a high pressure twin reactor system at the University of Veszprém department of Hydrocarbon and Coal Processing. This system consists of a tubular reactor of 100 cm³ efficient volume, as well as equipment and devices applied in the reactor system of hydrotreating plants (pumps,

Table 1 The emission limits of light duty diesel engines in the European Union

Standard	Emission limits, g/km				
	PM	NO _x	HC	CO	HC+NO _x
Euro 2 - 1996	0.080	-	-	1.06	0.71
Euro 3 - 2000	0.050	0.50	-	0.64	0.56
Euro 4 - 2005	0.025	0.25	-	0.50	0.30

Table 2 The present and the future quality requirements of diesel fuels

Requirements	EN 590 (2000)	EU (2005)	EU (2008/2009)	World Wide Fuel Charter, Category	
				3	4
Cetane number, min.	51	51	?	55	55
Density kg/m ³ , 15°C, max.	820-845	820-845	?	820-840	820-840
Polyaromatics, %, max.	11	11	?	2	2
Total aromatic content, %, max.	-	-	?	15	15
Distillation of 95lv% °C, max.	360	360	?	340	340
Sulphur content ppm, max.	350	50*	10	30	5-10

*From the year 2003 tax allowance in Germany for motor fuels having 10 ppm

separators, heat exchangers, temperature and pressure regulators, gas flow regulators), see Fig. 1.

The feedstock was a light gas oil fraction previously hydrodesulphurized to avoid the poisoning of the Pt/Al₂O₃ catalyst; its main properties before and after the treatment are given in Table 3.

The temperature range of the experiments was 180-300°C, the total pressure 40 bar; the liquid hourly space velocity (LHSV) varied between 0,5 h⁻¹ and 2,0 h⁻¹ and the volume ratio of hydrogen-to-hydrocarbon was 600 dm³/dm³.

The experiments were carried out on a Pt/γ-Al₂O₃ type catalyst having 0.58 % Pt-content.

The properties of the feedstock and products were determined by standard test methods: sulphur content by X-ray fluorescence spectrometry, aromatic content by HPLC.

The experiments were carried out on catalyst of permanent activity and by continuous operation. The repeatability of the experimental results was higher than 95% considering the ensemble errors of the technological experiments and test methods.

Table 3 The main properties of the feedstock before and after the hydrotreating

Properties	Method	Feed	
		untreated	treated
Density, 15°C, kg/m ³	ASTM D4052-96	826	816
Cetane number	MSZ EN ISO 5165	49	54.5
Cold Filter Plugging Point, CFPP, °C	MSZ EN 116	-	-30
Sulphur content, ppm	ASTM D2622-98	650	< 2
Aromatics, %	IP 391:1995		
Mono		8.8	9.9
Di		7.5	7.0
Poly		1.7	1.0
Total		18.0	17.9
Distillation data	ASTM D86-97		
Initial bp., °C		198	190
10 vol. %, °C		219	216
50 vol. %, °C		245	243
90 vol. %, °C		283	286
Final bp., °C		297	294
BMCI*		27.6	23.0

*Bureau of Mine Correlation Index

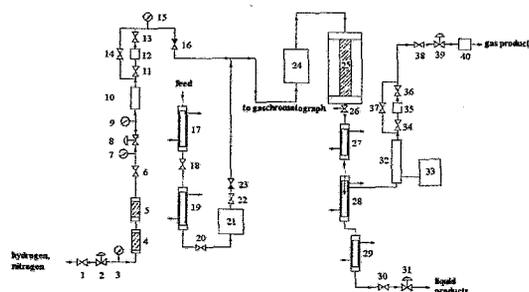


Fig. 1 The flow diagram of the reactor system; Notations: 1, 6, 11, 13, 14, 18, 20, 22, 30, 34, 36, 37, 38: closing valves; 2, 8, 31, 39: control valves; 3, 7, 9, 15: manometers, 4: oxygen converter; 5: dryer; 10, 32: gas filter; 12: gas flow meter/controller; 16, 23: back valve; 17, 19: liquid feeds burettes; 21: liquid pump; 24: pre-heater; 25: reactor; 26: sampling valve; 27, 29: cooler; 28: separator; 33: pressure recorder; 35: pressure controller; 40: wet gas flow meter

Results and Discussion

After the experiments we determined the yields of the liquid product which were above 99% in every case. These results showed that hydrocracking reactions take place only a little extent or not at all.

Fig. 2 displays the change of total aromatic content of the products as function of temperature and LHSV. It shows that both process parameters have significant effect on the saturation of aromatics.

Studying the effect of temperature on the reduction of aromatic content in case of LHSV 0.5 and 0.8 h⁻¹,

Table 4 Summary of the results of the advantageous experiments

Properties	Experiment			
	AM/1	AM/2	AM/3	AM/4
Process conditions				
Temperature, °C	280	280	300	300
Pressure, bar	40	40	40	40
LHSV, h ⁻¹	0.5	0.8	1.2	2.0
H ₂ /HC, dm ³ /dm ³	600	600	600	600
Yield, %	99.6	99.7	99.5	99.6
Product quality				
Density, kg/m ³	810	811	811	813
Sulphur content, ppm	< 2	< 2	< 2	< 2
Aromatics, %				
mono	0.5	1.6	2.9	3.6
di	0.08	0.09	0.1	0.4
poly	0.05	0.07	0.08	0.09
total	0.63	1.76	3.08	4.09
Distillation data, D86, °C				
initial bp.	185	186	187	187
10 vol.%	214	215	215	215
50 vol.%	241	242	242	243
90 vol.%	285	285	285	284
final bp.	294	294	295	296
Flash point, °C	78	78	78	79
Cetane number	57.5	57.0	57.0	56.5
CFPP, °C	-30	-30	-31	-31
BMCI	20.5	20.8	20.8	21.8

respectively, it can be assessed that the increase in temperature to about 280°C reduces the aromatic content to a minimum point and then it rises gradually.

It can be explained that from the point of view of kinetics the increase of temperature is advantageous for the saturation of aromatic rings until a point where thermodynamic hindrance, which arises from the exothermicity of the reaction, begins to exert a significant effect on the rate of reaction.

In case of higher LHSV 1.2 and 2.0 h⁻¹, respectively, we found that the aromatic content did not reach a minimum point, but it is expected that further increase in temperature would have the same effect.

Studying the effect of the LHSV it can be stated that lower LHSV, that is longer mean residence time, is favourable for reducing the aromatic content.

On the basis of experimental results we assessed that the maximum of the saturation of aromatics was in the temperature range of 280-300°C, within the applied process conditions (e.g. catalyst, feedstock, etc.). So the other properties of products obtained in this range were determined; the results are given in the Table 4.

These data display that the aromatic content of the products is significantly lower compared to the feedstock, that caused improve in other properties as well (e.g. cetane number), further the properties of the products meet all the demands of EN 590 standard.

Table 5 Emission potential of the products and feedstock

Emission, g/km	Feed		Experiment			
	untreated	treated	AM/1	AM/2	AM/3	AM/4
CO	1.230	1.201	1.185	1.188	1.188	1.194
HC	0.092	0.065	0.055	0.057	0.057	0.060
NO _x	0.920	0.918	0.917	0.917	0.918	0.918
PM	0.044	0.037	0.035	0.035	0.035	0.036

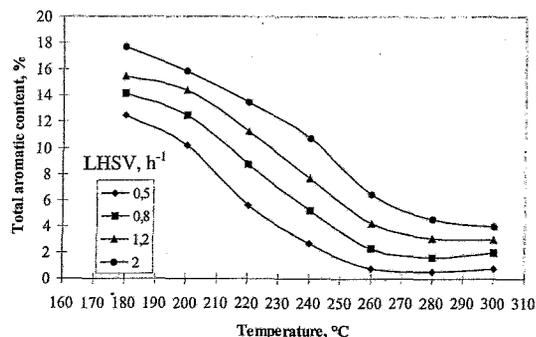


Fig.2 Effect of temperature and LHSV on the reduction of the total aromatic content

In addition the polyaromatic content and the cetane number of the products satisfy the EC limits which came into force in the year 2000 and the quality requirements of the World Wide Fuel Charter Categories 3 and 4.

We estimated the emissions of the products of the experiments. The equations approved by the EPEFE (European Programme on Emissions, Fuels and Engine Technologies) for the light duty diesel vehicles were used to determine the potential of emitting CO, hydrocarbon (HC), NO_x and particulate matter (PM) [18].

$$CO(g/km) = -1.3250726 + 0.003037 \cdot d - 0.025643 \cdot c_{PA} - 0.015856 \cdot CN + 0.0001706 \cdot T_{95} \quad (1)$$

$$HC(g/km) = -0.293192 + 0.0006759 \cdot d - 0.0007306 \cdot c_{PA} - 0.0032733 \cdot CN - 0.000038 \cdot T_{95} \quad (2)$$

$$NO_x(g/km) = 1.0039726 - 0.0003113 \cdot d + 0.027263 \cdot c_{PA} - 0.0000883 \cdot CN - 0.0005805 \cdot T_{95} \quad (3)$$

$$PM(g/km) = [-0.3879873 + 0.0004677 \cdot d + 0.0004488 \cdot c_{PA} + 0.0004098 \cdot CN + 0.0000788 \cdot T_{95}] \cdot [1 - 0.00016 \cdot (450 - c_s)] \quad (4)$$

where

$$d \quad - \text{density, kg/m}^3$$

$$c_{PA} \quad - \text{polyaromatic content, \%}$$

CN - cetane number
 T₉₅ - back-end volatility, °C
 c_s - sulphur content, ppm.

The data concerning the products and the feedstock are summarized in *Table 5*. On the basis of these data we established that reduction of the aromatic and sulphur content significantly contributes to the decrease of emission, except NO_x.

On the basis of these data it can be assessed that production of good quality diesel fuel blending components is only possible by using HDS and HDA processes together.

To determine the applicability of the products as base stocks of the steam cracking we applied the Bureau of Mine Correlation Index (BMCI), see *Eq.(5)*, which refers to the hydrocarbon types in the petroleum products. Polyaromatic hydrocarbons have the highest BMCI values (above 100) and paraffin hydrocarbons the smallest ones (below 20).

$$BMCI = \frac{48640}{VABP} + 473.7 \cdot d_{15.6}^{15.6} - 456.8 \quad (5)$$

where

VABP - volume average boiling point, K
 d_{15.6}^{15.6} - density, g/cm³

The decrease in BMCI value of the products showed the saturation of the aromatic, mainly the polyaromatic compounds, that improves the quality of the products from the aspect of applying them as base stocks of steam cracking.

Conclusions

We were able to produce diesel fuel blending components on the applied catalyst which satisfy the present (year 2000) and the future (year 2005) requirements.

The aromatic content of the feedstock can be reduced in one step to a great extent, and this decreases significantly the tailpipe emission of the diesel engine, except NO_x content.

The obtained product is applicable as diesel fuel blending component in itself or together with others in order to suit the standard specifications of commercial products that contributes to the reduction of emission of diesel engines.

The obtained products are applicable as good and less expensive base stocks of steam cracking.

SYMBOLS

LHSV liquid hourly space velocity
 HDA hydrodearomatization
 HPLC high performance liquid chromatography

CFPP cold filter plugging point
 BMCI Bureau of Mine Correlation Index
 HC hydrocarbon
 PM particulate matter
 d density
 c_{PA} polyaromatic content
 c_s sulphur content, ppm
 CN cetane number
 T₉₅ back-end volatility

REFERENCES

1. MCARRAGHER J. S.: Fuel Quality, Vehicle Technology and Their Interaction, CONCAWE, Brussels, 1999
2. PURMOR, P. D.: Mineralöltechnik, 1996, 2, 1-23
3. AAMA, ACEA, JAMA: World-Wide Fuel Charter, 2000
4. HANCSÓK J.: Fuels for Engines and Jet Engines, 2nd Part: Diesel Fuels, Veszprém University Press, Veszprém, 1999
5. PUNDIR B. P.: Diesel Fuel Quality for Low Emissions., 3rd International Colloquium on Fuels, Esslingen, pp. 239-245, 2001
6. LEE C. K. and MCGOVERN S.: Petroleum Technology Quarterly, 2001, 6(4), 35-40
7. SHELEF M. and MCCABE R. W.: Catalysis Today, 2000, 62, 35-50
8. SIGNER M.: Fuel Quality Influence on Engine Performance and Emissions, 3rd Annual World Fuels Conference, Brussels, 1998
9. FARRAUTO R. J. and HECK R. M.: Catalysis Today, 2000, 55, 179-187
10. VARGA Z., HANCSÓK J. and TOLVAJ G.: Investigation of the deep hydrodesulfurization of gas oil fractions, 40th International Petroleum Conference, Bratislava, 2001
11. TOCK R. W.: World Refining, 1999, 9(2), 53-62
12. ABD-ALLA G. H.: Energy Conversion and Management, 2002, 43, 1027-1042
13. HANCSÓK J., VALASEK I. and LAKATOS I.: Fuels and their use, Tribotechnik Kft., Budapest, 1998
14. PÁL R.: MOL Professional and Science Papers, 1998, (1), 168-181
15. JUNGBLUTH H. and RICHTER B.: Regeneration von Partikelfiltern mit Additiven, 2nd International Colloquium on Fuels, Esslingen, 9.4, 1999
16. HANCSÓK J.: Production of middle distillates of low aromatic content, Transactions of the University of Veszprém Department of Hydrocarbon and Coal Processing, 1997
17. HILLIER W. J.: Petroleum Technology Quarterly, 1998, 3(4), 39-44
18. MACKINVEN R. and MCARRAGHER J. S.: Review of the European Auto/Oil Programme and EPEFE, 1st International Colloquium on Fuels, Esslingen, 1.3, 1997